ARC SPECTRA AND IONIZATION POTENTIALS IN DISSOCIATED GASES.

By K. T. COMPTON,

(*Read April 21, 1922*)

The great complexity of spectra is due, in part, to the fact that the molecules may exist in various states of association, dissociation, and ionization, each type of molecule or atom giving rise to its own characteristic spectrum. A discovery of the exact state of the atom or molecule giving rise to each part of the spectrum of a substance is of great importance as regards both the theory of spectral emission and the theory of atomic and molecular structure. At the Palmer Physical Laboratory this problem is being attacked from three different angles. This paper presents some discoveries made by two of these methods and discusses their significance.

Hydrogen.

Bohr's theory is believed satisfactorily to account for the known properties of hydrogen atoms. Hydrogen ordinarily exists, however, in the form of diatomic molecules, whose properties have not been adequately explained by any hypothesis of molecular structure yet proposed. Those properties of the hydrogen atom which Bohr's theory explains are the series spectrum and the energy required to produce radiation or to ionize the atoms, commonly expressed as radiating and ionizing potentials, respectively. Other radiating and ionizing potentials and another type of spectrum are believed to be due to hydrogen molecules. In no case has there been direct and definite evidence as to which type of spectrum is due to the atom and which to the molecule, although sufficient indirect evidence is at hand to ascribe the series spectrum to the atom and the secondary spectrum to the molecule with considerable certainty. There has been no experimental evidence at all as to which entity to ascribe each radiating or ionizing potential observed in hydrogen. The assignment of

particular critical potentials to atom or molecule has been justified by the degree of consistency with probable processes of dissociation, radiation, or ionization. The present investigations have yielded definite and direct experimental evidence on the above points and have thrown new light on the nature of low voltage arcs and on the manner of excitation of the spectrum.

Low Voltage Arc in Hydrogen.

Dr. O. S. Duffendack has studied the relation of voltage to arc currents and spectral excitation. The arcs were produced in gas at pressures between 0.5 and 5.0 mm. between two electrodes, as shown in Fig. 1. *AB* was a tube of thin tungsten foil, which could be

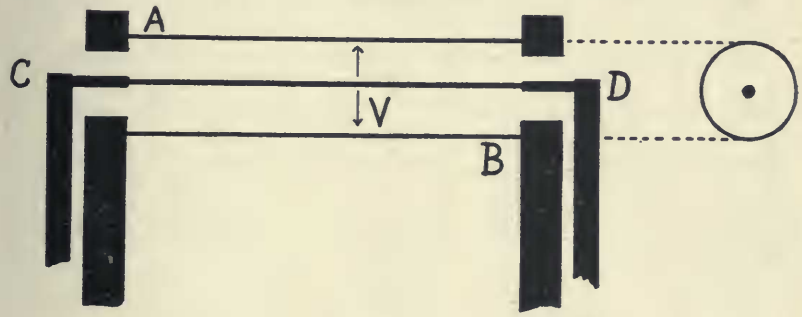

FIG. 1.

heated by a current through water-cooled leads. *CD* was a 20-mil tungsten wire passing axially through the tube and also electrically heated. The potential drops across the tube and the filament could be adjusted to practical equality, so that they behaved as equipotential electrodes to electrons emitted from the wire and drawn to the tube by an applied difference of potential *V*. The tube was 30 mm. long and of 3.7 mm. radius. Ionization of gas within the tube was detected by increase of current *I* between the electrodes, and the spectrum of the excited radiation was observed through an open end of the tube.

With the filament heated to a bright incandescence, but with the tube relatively cool, the current-voltage variation is illustrated by Fig. 2. From curve (*a*) it is seen that the current first is very small and increases slowly with voltage until the ionization potential, about

16.3 volts, is approached. Ionization is first detected a couple of volts below this because the electrons are emitted from the filament with small initial speeds. When the current has increased to a certain value, the arc strikes, with a sudden large increase in current, at a voltage higher than the minimum ionizing potential. As the voltage is then diminished the arc persists down to the minimum ionizing potential, but breaks at this voltage. If the filament is hotter, so as to emit more electrons, as in curve (*b*), the arc strikes at a voltage

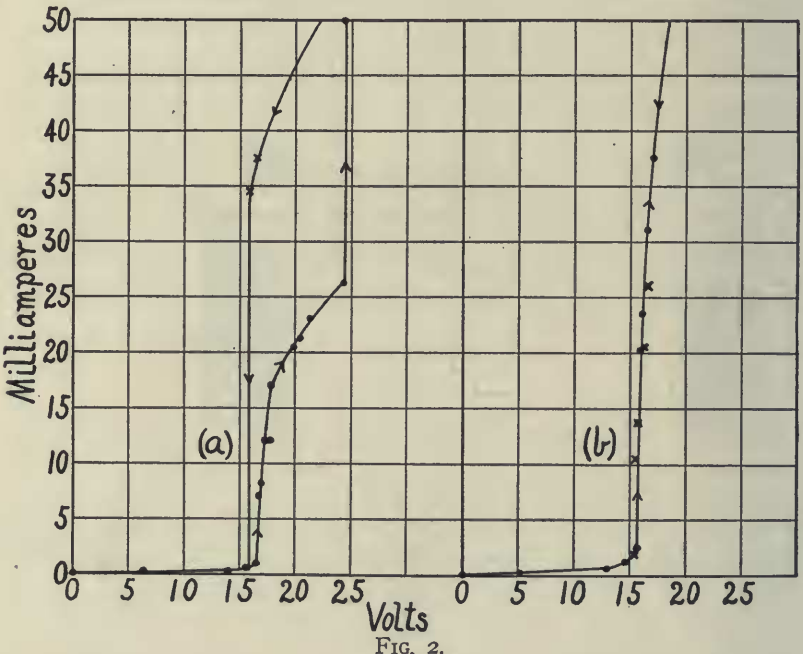

FIG. 2.

nearer the ionizing potential and still breaks at this voltage. In no case was it possible to produce or maintain the arc at a voltage less than the minimum ionizing potential, about 16.3, except for a very small amount depending on the temperature of the filament, due to the initial energy of emission, and easily allowed for.

When the outer tube was very hot, the conditions were quite different, as seen by Fig. 3. The initial current is larger, there is ionization beginning at about 10 volts, and stronger ionization at about 14 volts. In curve (*a*) the arc struck and was maintained at about 13.8

volts, while in curve (*b*), with the tube still hotter, the arc struck at about 10.0 volts, and there was no indication of further ionization near either 14 or 16 volts.

The essential difference between these two cases lies in the fact that in the latter cases the tube was sufficiently hot to completely dissociate the hydrogen inside it into atomic hydrogen. Thus the critical potential 16.3 is the ionization potential of hydrogen *molecules,* whereas 13.6 volts is that of hydrogen *atoms.* The critical potential, 10.1 volts, is also due to *atomic* hydrogen and is shown later to be

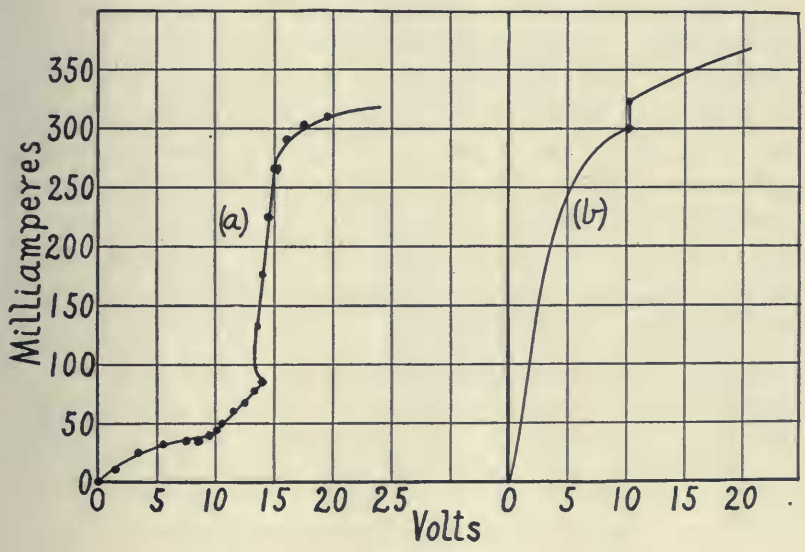

FIG. 3.

due to excitation of radiation from the atoms. That this radiation results in ionization is probably due to a "cumulative" effect—atoms being struck by electrons while they are in a partially ionized state because of absorption of energy of radiation from neighboring atoms.

The above experiments do not fix the values of the critical potentials as accurately as do the experiments by the following method, but they do determine beyond all question the sources of the observed effects. *These are the first laboratory experiments to be performed in an atmosphere of atomic hydrogen.*

Incidentally the character of the current-voltage curves yields knowledge of the processes which produce the arc. At voltages so low as to avoid ionization the current is due entirely to the electronic emission from the filament, and this is limited to a very small value, independent of the temperature of the filament, provided it is high, by the negative space charge of the electrons immediately surrounding it.[1] When ionization occurs each positive ion, drawn toward the filament, neutralizes the space charge of about 243 electrons and thus permits the escape of that additional number. This large number of electrons liberated by each positive ion is due to the relatively small speed with which the heavy positive ion moves through the region of space charge. The current increase is therefore due not so much to the addition of ions by ionization as to the effect of the positive ions in permitting the escape of many more electrons from the filament. Thus the current increases with increasing voltage until it approaches the thermionic saturation current characteristic of the size and temperament of the filament. Then there are no longer sufficient electrons to neutralize the effect of the positive ions near the filament so that the space charge changes from negative to positive, creating an accelerating field for the emitted electrons and giving the saturation thermionic current plus the ionization current. This is the arc. It is characterized by its sudden appearance and by the concentration of luminosity in the region very near the filament, where the principal portion of the potential drop occurs, with positive space charge.

Excitation of the Hydrogen Spectrum.

In molecular hydrogen there was no visible spectrum until the arc flashed in at or above 16.3 volts. Then there appeared the Balmer series lines and part of the secondary, or band, spectrum. The part appearing was Group I., of Fulcher's Classification,[2] which includes those lines which show little intensification with increasing voltage. These lines are also those which show no Zeeman effect and are apparently the ones which Merton found not to be enhanced by the admixture of helium with the hydrogen.[3]

[1] Langmuir, *Phys. Rev.*, 2, p. 543, 1913.
[2] *Astrophys. Jour.*, 37, p. 65, 1913.
[3] *Roy. Soc. Proc., A.*, 96, p. 382, 1919.

In atomic hydrogen the secondary spectrum was entirely absent, but the series spectrum appeared strongly when the arc struck at 13.5 volts and could be detected down to 10.1 volts.

These results confirm the prevailing opinion that the series spectrum is due to atoms and the secondary spectrum is due to molecules. The voltages at which the spectrum appears in atomic hydrogen are exactly those to be expected from Bohr's interpretation of the series formula. The exciting voltage in molecular hydrogen is that to be expected if the critical 16.3 voltage is interpreted as dissociation of the molecule plus ionization of one of the atoms as the result of single electron impacts, giving $16.3 - 13.5 = 2.8$ volts as the heat of dissociation in equivalent volts. This is almost exactly the value given by Bohr's theory, but is lower than the value 4.06 volts calculated from Langmuir's measurement of the heat of dissociation of hydrogen.[4]

The interpretation of the secondary spectrum is puzzling. It is certainly due to molecular hydrogen, but the nature of the emitting molecule is uncertain. It is probably not due to neutral H_2 molecules, since these have no absorption in the visible spectrum. $\dot{H}_2$ molecules are known to be present in fairly large concentration in an arc, but more in a high voltage discharge in a large vessel at low pressures. H_3 molecules are also known to be present. Possibly one of these may give rise to Fulcher's Group I. and the other to his Group II., but evidence on this point is rather conflicting. An observation of possible interest in this connection is that we found the secondary spectrum to disappear, when the outer tube was heated, at temperatures certainly too low to have dissociated H_2 molecules to any great extent. This suggests that the molecule responsible for the observed secondary spectrum lines is less stable than H_2. As far as this is concerned, it may be either $\dot{H}_2$ or H_3. The absence of a Doppler shift for these lines may possibly point to the neutral H_3 molecule as the agent. In this connection it may be mentioned that R. W. Wood has very recently succeeded in drawing off pure atomic hydrogen from the center of a long Geissler tube, where only the series spectrum is visible, and he finds that the presence of a tungsten

[4] *Am. Chem. Soc. Jour.*, 37, p. 417, 1915.

wire in this stream causes the atoms to recombine at its surface, with the emission of the secondary spectrum and a heating of the wire.*

Further Critical Potentials in Hydrogen.

The problem has been attacked from another angle by Dr. P. S. Olmstead, who used a modification of the Lenard method of investigating ionization potentials, illustrated in Fig. 4. Electrons from the

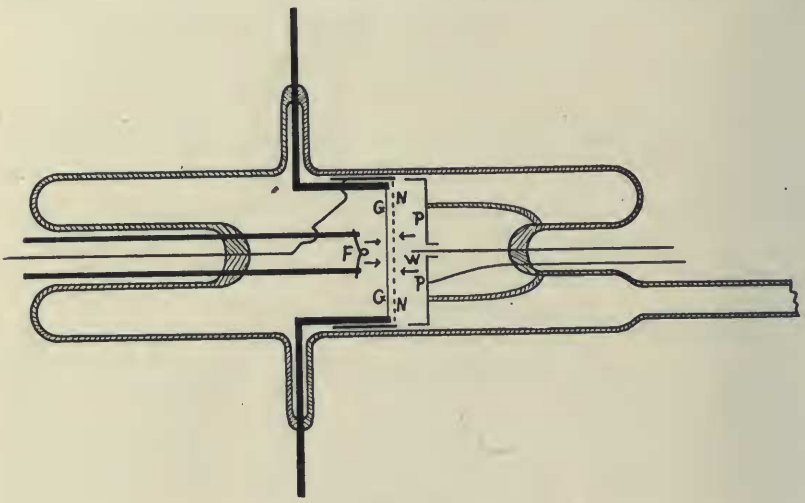

FIG. 4.

hot central portion of a tungsten filament F were drawn toward a wire net NN through an accelerating difference of potential V. Those which passed the net NN encountered a retarding field V_r sufficient to stop them.

The two distinctive features of the apparatus were the system of detecting electrodes P and W and a grid GG of twenty parallel tungsten wires. PP was a platinum plate and W was a fine platinum wire extending but a short distance in front of the plate PP. When the electrons from F collided with and produced radiation from atoms or molecules near the net NN a considerable amount of this radiation fell on the plate PP, whereas the wire W received only a negligible amount of radiation because of its very small area. Either PP or W

* Since this paper was written very decisive evidence on these points has been obtained and is to be published by Dr. Duffendack in the Astrophys. Jour.

could be connected to the quadrant electrometer, which measured both the current due to ionization of the gas between *NN* and *PP* and the photoelectric current from *PP* or *W* due to the radiation set up by electron bombardment of the gas. Those effects, setting in at critical potentials which were due to radiation, were relatively more pronounced when the plate *PP* was joined to the electrometer. Effects of ionization were relatively more marked when the wire *W* was used, since this wire could collect all the positive ions formed, but would receive but little of the radiation.

The grid *GG* was used to vary the proportion of atomic hydrogen in the neighborhood of the net *NN*. This was done by heating it to a high temperature by an electric current, if atomic hydrogen was desired. The relative proportion of atomic to molecular hydrogen was never large, but was sufficient for our purpose. Those critical potentials which were relatively more marked when the grid *GG* was hot were ascribed to atomic hydrogen and the others to molecular hydrogen.

By thus varying the sensitiveness to detection of radiation, and by varying the amount of atomic hydrogen present, it was possible definitely to determine the nature and origin of the effect setting in at each of the critical potentials of hydrogen.

The critical potentials are shown by Fig. 5, taken with the plate *PP* joined to the electrometer, and with the grid *GG* hot. Similar curves with the wire *W*, or with the grid cold, show fewer "breaks," as expected. The interpretation of these critical potentials is indicated by the "ratio" curves of Fig. 6. These curves show ratios of electrometer deflections under the various conditions. *I* (on)/*I* (off) means the ratio of the deflections using the wire *W* (relatively sensitive to effects of ionization) with the grid current on (hot) and off (cold) respectively. *R* (on)/*I* (on) means the ratio of the deflections with the plate (relatively sensitive to radiation) to those with the wire (relatively sensitive to ionization), the grid current being on in both cases. When these curves are interpreted in the light of the discussion above, and when proper allowance is made for the effect of the initial velocities with which electrons are emitted from the filament (which introduces a small correction for weak effects and a

larger one for strong effects), the interpretation of each of the critical potentials is as shown in Table I. Setting in of new effects produces a change in curvature of the curves of Fig. 6. Such changes do not necessarily indicate new effects, however, and the effects may not be shown prominently at exactly the same voltage as in Fig. 5. Some caution is needed, therefore, in interpreting the curves in cases which

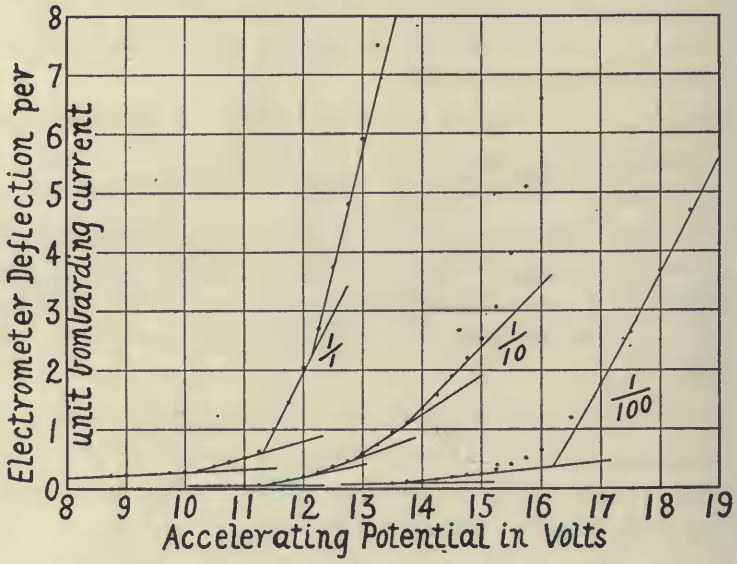

FIG. 5.

correspond to weak effects. We believe, however, that a consideration of the full set of curves points unmistakably to the following results:

TABLE I.

Critical Potential.	Nature.	Due to	Process.
10.1 volts....	Radiation	Atom	Direct
11.3.....	Ionization	Molecule	Ionization without dissociation
12.1.....	Radiation	Atom	Direct
12.8	Radiation	Molecule	Dissociation plus radiation from an atom
13.6.....	Ionization	Atom	Direct
16.2.....	Ionization	Molecule	Dissociation plus ionization of an atom

As an example of the method of interpretation, consider the 13.6 volt effect. The R (on)/I (on) curve indicates that it is due to ionization. The I (on)/I (off) curve indicates that it is due to the

but do not give such decisive information. The above critical potenatom. The other two curves are consistent with these interpretations,

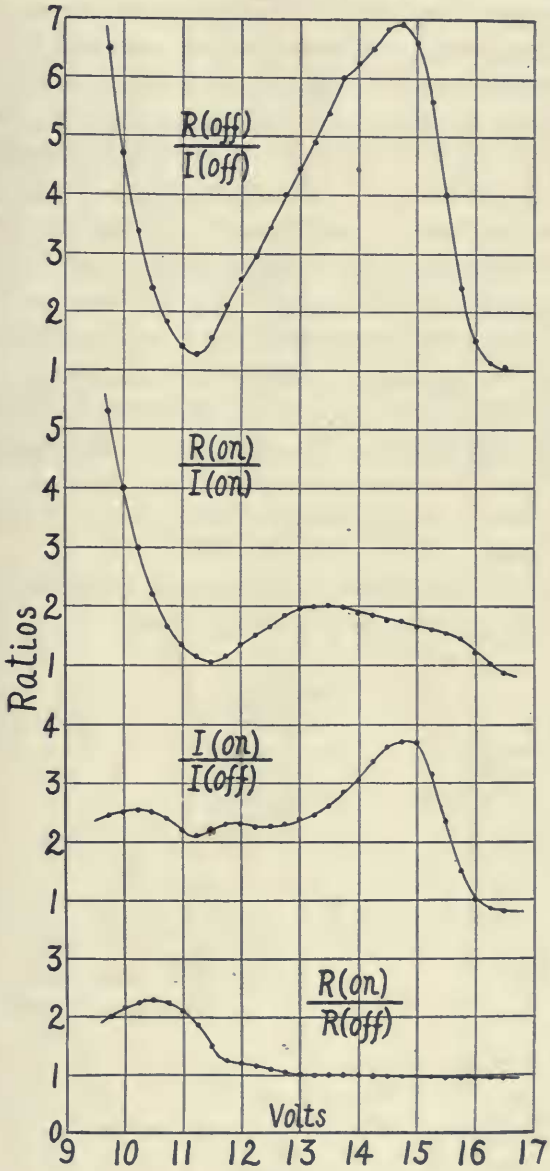

FIG. 6.

tials are determined experimentally to within probably 0.2 volt, when the corrections for velocity distribution are considered.[5]

The three atomic effects correspond exactly, by the quantum relation $eV = h\nu$ to the first two lines 1216 Å. and 1026 Å. and to the convergence wave length 911 Å. of the Lyman series. This is, I believe, the first time that evidence has been obtained for the excitation of the second member of the series separately. We have some evidence of the separate excitation of the third member, also, and are setting up a new apparatus designed to detect atomic radiation effects very sensitively, with entire freedom from effects of ionization. With this we expect to make a more thorough investigation of the excitation of the successive members of the Lyman series.

The 11.3 volt molecular effect is the formation of $\overset{+}{H}_2$, an ion which is found by positive ray analysis to be very abundant, although Bohr's theory of the molecule represents it as unstable. The 12.8 and 16.2 volt effects correspond to the processes $H_2 = H + H_r$ and $H_2 = H + \overset{+}{H}$, respectively. The heat of dissociation is given, in equivalent volts, by $12.8 - 10.1 = 2.7$ volts or by $16.2 - 13.6 = 2.6$ volts. This is in good agreement with the results of the preceding method, but smaller than Langmuir's value.

The critical potentials reported by previous observers are given in Table II. The considerable lack of consistency among the various

TABLE II.

Experimenter	Radiation			Ionization			
Davis and Goucher [6]	11.0,		13.6,	11.0,		15.8	
Mohler and Foote [7]	10.4,	12.2,			13.3,	16.5	
Foote, Mohler and Kurth [8]	10.5,	11.8,				16.0	
Horton and Davies [9]	10.5,		13.9,		14.4,	16.9	
Franck, Knipping and Krüger [10]			13.6,	11.5,		17.1,	30.45
Compton and Olmstead [11]	<10.8,		13.4,	>10.8,		>15.8	
Boucher [12]	10.1,				13.6,	15.6	
This Investigation	10.1,	12.1,	12.8,	11.3,	13.6,	16.2	

[5] Smyth, *Phys. Rev.*, 14, p. 409, 1919; Compton and Olmstead, *Phys. Rev.*, 17, p. 52, 1921.

[6] *Phys. Rev.*, 10, p. 101, 1917.

[7] *Jour. Optical Soc. of Am.*, 4, p. 49, 1920.

[8] *Phys. Rev.*, 19, p. 414, 1922.

[9] *Roy. Soc. Proc., A*, 97, p. 23, 1920.

[10] *Ber. d. D. Phys. Ges.*, 21, p. 728, 1920.

[11] *Phys. Rev.*, 17, p. 45, 1921.

[12] *Phys. Rev.*, 19, p. 189, 1922.

critical potentials reported is probably due to (1) the fact that the velocity distribution correction is likely to be exaggerated for the stronger effects, unless a systematic method such as was suggested by Smyth or its graphical equivalent is used, (2) two effects occurring close together are likely to be reported as one, (3) the form of apparatus may be such as to enhance ionization effects relatively to radiation effects, or vice-versa.

Nitrogen.

This gas has been studied by Dr. Duffendack, using the low voltage arc method as in the case of hydrogen. It was found that the gas could not be appreciably dissociated into atomic nitrogen by any attainable temperature of the tungsten tube furnace, although it was possible to produce atomic nitrogen (Strett's "active" nitrogen)[13] by electronic bombardment at lower current densities and voltages when the tube was very hot than when it was cooler.

Low Voltage Arc in Nitrogen.

Typical current-voltage curves are shown in Fig. 7. In curve

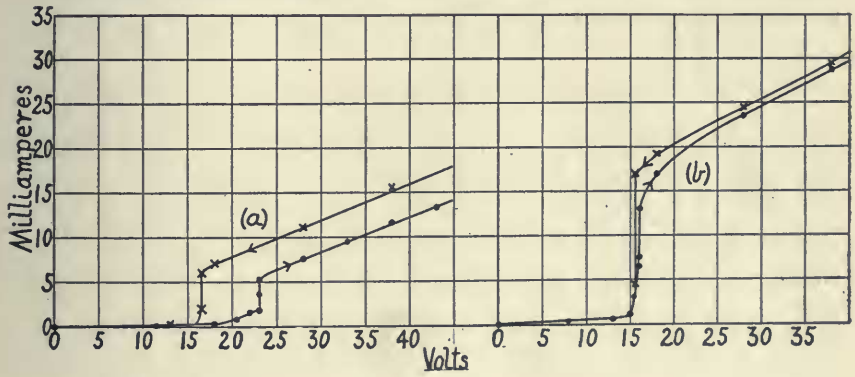

Fig. 7.

(*b*) the filament was hotter and the gas pressure lower than in curve (*a*), both conditions favoring the production of the arc. The "break" point of the arc was found to be 16.15 volts as an average of a large number of closely agreeing observations made under various experimental conditions. Under no conditions could the arc be

[13] *Roy. Soc. Proc., A,* 85, p. 219, 1911, et seq.

maintained at a voltage lower than this, which is the minimum ionizing potential of the molecule.

The shape of these curves differs from that of the hydrogen arc curves in that the current rapidly increases with increasing voltage above the arcing voltage. This is probably due to the greater complexity and stability of the molecule, since it seems to be related to the rapid increase of intensity of the negative band spectrum as the voltage is increased. This negative band spectrum is due, as shown by its behavior in a positive ray apparatus and its relation to exciting voltage, to excitation of the positively charged molecules N_2^+, which can evidently be partially or completely ionized without breaking up into atoms.

In the neighborhood of 70 volts the arc current began to increase rapidly again, a brilliant "flare" setting in and the current becoming as large as 15 amperes. Simultaneously with this increase the lines 5006 and 5003 of the nitrogen line spectrum appeared. At about 90 volts the lines 5680 and 5667 were visible. If the filament is hot, this "flare" could be maintained at voltages as low as 25 volts, after setting in at 70 volts, but no lines of the line spectrum were seen below 70 volts. Lines of the tungsten spectrum were always observed in the flare.

Comparison with observations by Strutt[14] shows that this flare was due to the presence of *atomic* nitrogen, and that the presence of the tungsten spectrum was due to the burning of tungsten in atomic nitrogen. It is significant that the flare could be produced at 40 volts, instead of 70 volts, if the outer tungsten tube were very hot. This is the only evidence of dissociation of nitrogen by the hot tube. It is also of interest to note that Langmuir discovered an anomalous behavior of thermionic emission from tungsten filaments in nitrogen at low pressures and voltages above 70 volts, and attributed this to a chemical action which did not occur at lower voltages.[15] It is not easy to explain why the formation of atomic nitrogen should increase the current through the arc so enormously. Multiple ionization, ionization by chemical action on tungsten, or heat developed by atomic recombination at the surface of the filament may be important factors.

[14] *Loc. cit.*

[15] *Phys. Rev.*, 2, p. 450, 1913.

Excitation of the Nitrogen Spectrum.

The nitrogen spectrum consists of three groups of positive bands, two of which appear in the visible spectrum and one only in the ultra-violet, a group of negative bands and a line spectrum which has not been resolved into series.

The first group of positive bands was first seen when the arc struck and increased slightly in intensity as the voltage was raised. The second group was first seen when the arc struck and decreased in intensity with increasing voltage. L. and E. Bloch[16] and Brandt[17] have detected positive bands at voltages as low as 12 and 7.5 volts, respectively. It is therefore evident that the positive bands are due to excitation of neutral molecules.

The negative bands were not observed until the voltage was a volt or two above the minimum ionizing potential, and increased markedly in intensity with increasing voltage. Rau[18] has found a Doppler shift in the negative bands in positive rays. These and other facts indicate that the negative bands are due to excitation of positively charged molecules $\dot{N}_2$.

It is surprising that as high a voltage as 70 volts was required to excite the line spectrum, and that only the lines 5006, 5003, 5680, and 5667 were observed. There are a number of other lines usually listed as at least as intense as these of which no trace was found. It seems probable, as is suggested by the magnitude of the Doppler shifts[19] for the nitrogen lines, that the lines which we observed are enhanced lines, and the remaining strong lines in the visible spectrum may correspond to still higher ionization. The Doppler shifts suggest that a line 3995 Å. may be an unenhanced line. Unfortunately we did not investigate this region of the spectrum, but we plan to make a photographic test in the near future. At any rate, it seems certain that the simpler parts of the nitrogen line spectrum lie in a region of wave-lengths far removed from the visible, and that the difficulty of dissociating the molecules makes it difficult to excite the line spectrum under conditions which can easily be interpreted.

[16] *Comptes Rendus*, 170, p. 1380, 1920.
[17] *Zeit. f. Phys.*, 8, p. 32, 1921.
[18] "Vortrag auf der Physikertagung in Jena," 1921.
[19] J. J. Thomson, "Positive Rays."

Summary.

These investigations open up new methods for the study of conditions of dissociation, ionization, and excitation of radiation of multiatomic molecules. They have given a definite interpretation to the critical potentials of hydrogen and yielded valuable information regarding the processes of ionization and radiation in nitrogen. Similar work with iodine is in progress.

Palmer Physical Laboratory,
Princeton, New Jersey.